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(54)【発明の名称】 層状ペロブスカイト化合物、窒素酸化物浄化触媒材料及びこれを用いた排ガス浄化用触媒

(57)【要約】

【課題】 硫黄被毒を生ずる環境下において、600℃未満の温度領域及び酸化雰囲気下でも高いNO_x浄化能を有し、且つ十分な耐硫黄被毒性を有する層状ペロブスカイト化合物、窒素酸化物浄化触媒材料及びこれを用いた排ガス浄化用触媒を提供すること。

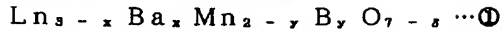
【解決手段】 一般式①

$Ln_{1-x}Ba_xMn_{2-y}B_yO_{7-\delta} \cdots ①$

(式中のLnは少なくとも1種のランタノイド元素、Bは3d遷移元素から成る群より選ばれた少なくとも1種の元素、 $1.8 < x < 2.8$ 、 $0.2 < y < 1.5$ 、 $5.5 \leq \delta < 7.0$ を示す。)で表されることを特徴とする層状ペロブスカイト化合物である。この層状ペロブスカイト化合物を含有する窒素酸化物浄化触媒材料、及び排ガス浄化用触媒である。

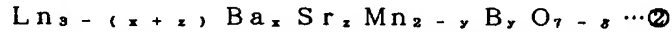
【特許請求の範囲】

【請求項1】 次の一般式①



(式中のLnは少なくとも1種のランタノイド元素、Bは3d遷移元素から成る群より選ばれた少なくとも1種の元素、 $1.8 < x < 2.8$ 、 $0.2 < y < 1.5$ 、 $5.5 \leq \delta < 7.0$ を示す。)で表されることを特徴とする層状ペロブスカイト化合物。

*



(式中のLnは上記と同じ元素(但し、ストロンチウムを除く)、Bは上記と同じ元素、 $1.8 < x+z < 2.8$ 、 $0 < z < 0.5$ 、 $0.2 < y < 1.5$ 、 $5.5 \leq \delta < 7.0$ を示す。)で表されることを特徴とする請求項1又は2記載の層状ペロブスカイト化合物。

【請求項4】 請求項1〜4のいずれか1つの項に記載の層状ペロブスカイト化合物を含有して成ることを特徴とする窒素酸化物浄化触媒材料。

【請求項5】 酸素過剰雰囲気下における排ガス中の一酸化炭素、炭化水素及び窒素酸化物を同時に浄化し得る排ガス浄化用触媒において、多孔質担体に、請求項4記載の窒素酸化物浄化触媒材料と白金及び/又はパラジウムとを担持して成ることを特徴とする排ガス浄化用触媒。

【発明の詳細な説明】

【0001】

【発明が属する技術分野】本発明は、層状ペロブスカイト化合物、窒素酸化物浄化触媒材料及びこれを用いた排ガス浄化用触媒に係り、更に詳細には、特定の組成・構造を有する複合酸化物であって、酸素過剰雰囲気及び還元雰囲気下でNO_xを吸収浄化し得る性質を有する層状ペロブスカイト化合物、これを用いた窒素酸化物浄化触媒材料及び排ガス浄化用触媒に関し、特に、内燃機関の運転又は天然ガスの燃焼によって排出される排気ガスの浄化や工場等における化学工程で発生するNO_xの吸着及び脱硝工程などに有効である。

【0002】

【従来の技術】ペロブスカイト型構造を有する材料は、理想的には立方晶系に属するが、正方晶系、斜方晶系及び六方晶系等に属するひずんだ構造を採ることが多く、このひずみにより生ずる双極子モーメントのために強誘電性を示すなど、種々の興味ある電磁気特性を示す。このため、従来から電磁気材料として種々研究されており、誘電体、磁気抵抗素子、ガスセンサー及び電極、特に固体電解質用電極等の材料として検討されており、また、強誘電体であるBaTiO₃、KTaO₃やKNbO₃等の単結晶は、電気光学用材料として注目されている。

【0003】近年では、各種ペロブスカイト材料を層状化する等して、優れた特性を有するペロブスカイト化合物を合成する試みもなされており、これらの中には、後

*【請求項2】 上記一般式①のLnがランタン、ネオジウム、サマリウム、ガドリニウム、イットリウム及びストロンチウムから成る群より選ばれた少なくとも1種の元素であり、Bが鉄、コバルト及びアルミニウムから成る群より選ばれた少なくとも1種の元素であることを特徴とする請求項1記載の層状ペロブスカイト化合物。

【請求項3】 次の一般式②

述するように、窒素酸化物を吸収し、酸素と窒素に分解して放出することから、排ガスの浄化において注目されているものもある。

【0004】また、従来から内燃機関の排気ガスを浄化する触媒としては、自動車用排ガス浄化触媒に代表されるように、例えば、コーゼライト等の耐熱性担体にγ-アルミナスラリーを塗布後焼成して、白金(Pt)、パラジウム(Pd)及びロジウム(Rh)等の貴金属を担持した排ガス浄化用三元触媒が典型的であり、広く知られている。

20 【0005】更に近年、地球規模での環境に対する意識の高まりから、内燃機関の燃焼効率の改善や燃費向上、排気ガスの浄化等に対して質・量ともに要求水準が上がってきている。このような状況から、特に内燃機関の燃焼を改善することが研究されており、現在、酸素過剰の混合気で燃焼を行う希薄燃焼(リーン)領域での運転がさかんに行われ、このリーン領域においてもNO_xを十分に浄化できる触媒が望まれている。

30 【0006】かかるリーン領域においても十分にNO_xを浄化する方法としては、(1)リーン雰囲気下、気相中の炭化水素(HC)を利用してNO_xを浄化するゼオライト触媒を用いる方法(Machida, Murakami, Kijima; J. Mater. Chem., 4(1994)1621)と、(2)バリウム酸化物、ランタン酸化物及び白金を組み合わせ、リーン雰囲気下でNO_xを吸収し、三元領域で三元触媒によりNO_xを浄化させる方法(特開平5-511556号公報、特開平5-261287号公報)とが提案されている。

40 【0007】また、Machidaらは、上記(1)の文献において、La_{2-x}Ba_xSrCu₂O₆で表されるペロブスカイト複合酸化物が、NOの吸収とともに600℃以上の高温でこの吸収されたNOを酸素と窒素に分解して放出することを報告している。更に、上記(2)の文献においては、酸素過剰雰囲気下の排ガスの浄化に、アルカリ金属、アルカリ土類金属、希土類元素から成るNO_x吸収剤と貴金属触媒を組み合わせることで、酸素過剰雰囲気下でのNO_x浄化性能が得られることが開示されている。

50 【0008】なお、「新しい配位子場の科学(講談社サイエンティフィク、1998)田辺行人監修 菅野暁、三須明、品田正樹、山口豪編」においては、遷移金属化

合物の電子構造、化学結合が記載されており、特に第三章（藤森淳著）では、ペロブスカイト複合酸化物に関する電子状態が明らかにされている。

【0009】

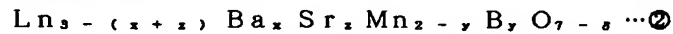
【発明が解決しようとする課題】しかしながら、上記（1）の方法で使用される従来のペロブスカイト複合酸化物は、600℃以上の温度領域では、NO_xの吸着と同時に放出が顕著になり、NO_x吸収量の減少を生じてしまうという課題があった。

【0010】また、上記（2）の方法で使用されるアルカリ金属等から成るNO_x吸収剤と貴金属との組合せに係る従来の排ガス浄化触媒では、650℃以上の加熱耐久で十分なNO_x吸収量を得るために添加（担持）されたアルカリ金属成分が担体と反応して劣化するという課題があった。

【0011】更に、従来の排ガス浄化触媒は、特にディーゼルの燃焼では、排出ガス中に硫黄酸化物（SO_x）ガスが含まれるので、硫黄被毒を受けることが知られており、上記（2）の文献の場合のように、バリウム酸化物等がNO_x吸収作用を担う場合には、SO_xガスによる硫黄被毒が顕著であり、NO_x浄化性能が著しく低下するという課題があった。

【0012】なお、上述のバリウム酸化物をLa_{0.7}Ba_{0.2}Mn_{0.8}Co_{0.2}O_{3-δ}のようなペロブスカイト複合酸化物とすることにより、Baを安定化することも可能であるが、本発明者らは、この場合であってもSO_xガスによってNO_x浄化性能が著しく低下することを知見した。更に、本発明者らは、Machidaらが提案したLa_{2-x}Ba_xSrCu₂O₆においても、SO_xガスによる硫黄被毒が顕著であることも知見した。

【0013】以上のように、従来の酸化物系触媒では、使用可能な温度領域が狭い外、これらを用いたNO_x吸着においては、硫黄被毒によってNO_x吸収量が著しく*



（式中のLnは上記と同じ元素（但し、ストロンチウムを除く）、Bは上記と同じ元素、1.8<x+z<2.8、0<z<0.5、0.2<y<1.5、5.5≤δ<7.0を示す。）で表されることを特徴とする。

【0018】また、本発明の窒素酸化物浄化触媒材料は、上述の如き層状ペロブスカイト化合物を含有して成ることを特徴とする。

【0019】更に、本発明の排ガス浄化用触媒は、酸素過剰雰囲気下における排ガス中の一酸化炭素、炭化水素及び窒素酸化物を同時に浄化し得る排ガス浄化用触媒において、多孔質担体に、上述の如き窒素酸化物浄化触媒材料と白金及び／又はパラジウムとを担持して成ることを特徴とする。

【0020】

【発明の実施の形態】以下、本発明の層状ペロブスカイ

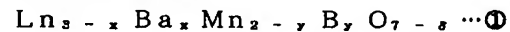
*減少する。このため、種々の使用環境において幅広い温度領域及び雰囲気下でNO_x浄化性能を発揮する排ガス浄化触媒材料や排ガス浄化用触媒が望まれていた。

【0014】本発明は、このような従来技術の有する課題に鑑みてなされたものであり、その目的とするところは、硫黄被毒を生ずる環境下において、600℃未満の温度領域及び酸化雰囲気下でも高いNO_x浄化能を有し、且つ十分な耐硫黄被毒性を有する層状ペロブスカイト化合物、窒素酸化物浄化触媒材料及びこれを用いた排ガス浄化用触媒を提供することにある。

【0015】

【課題を解決するための手段】本発明者らは、上記課題を解決すべく鋭意研究を重ねた結果、特定の組成・構造を有する新規な層状ペロブスカイト化合物が600℃未満の温度領域及び酸化雰囲気下でも高いNO_x浄化能を有し、且つ十分な耐硫黄被毒性を有することを見出し、上記課題が解決されることを見出し、本発明を完成するに至った。

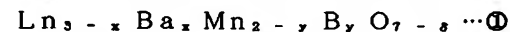
【0016】即ち、本発明の層状ペロブスカイト化合物は、次の一般式①



（式中のLnは少なくとも1種のランタノイド元素、Bは3d遷移元素から成る群より選ばれた少なくとも1種の元素、1.8<x<2.8、0.2<y<1.5、5.5≤δ<7.0を示す。）で表されることを特徴とする。また、本層状化合物においては、一般式①のLnがランタン、ネオジウム、サマリウム、ガドリニウム、イットリウム及びストロンチウムから成る群より選ばれた少なくとも1種の元素であり、Bが鉄、コバルト及びアルミニウムから成る群より選ばれた少なくとも1種の元素であることが好ましい。

【0017】また、本発明の層状ペロブスカイト化合物の好適形態は、次の一般式②

ト化合物について詳細に説明する。以上の如く、本発明の層状ペロブスカイト化合物は、次の一般式①

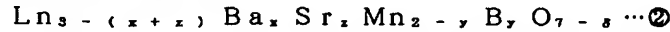


（式中のLnは少なくとも1種のランタノイド元素、Bは3d遷移元素から成る群より選ばれた少なくとも1種の元素、1.8<x<2.8、0.2<y<1.5、5.5≤δ<7.0を示す。）で表され、通常のペロブスカイト複合酸化物や銅系層状ペロブスカイト酸化物、又は酸化物混合系NO_x吸収触媒材料に比し、優れた耐硫黄被毒性を有し、600℃未満の温度領域でもNO_xを有効に浄化でき、耐久性も良好である。

【0021】ここで、一般式①のLn（ランタノイド元素）としては、La（ランタン）、Nd（ネオジウム）、Sm（サマリウム）、Gd（ガドリニウム）、Y（イットリウム）又はSr（ストロンチウム）及びこれ

らの任意の組合せが好ましく、B(3d遷移元素)としては、Fe(鉄)、Co(コバルト)又はAl(アルミニウム)及びこれらの任意の組合せが好ましい。

【0022】また、xが1.8以下では、十分なNO_x吸収性能が得にくく、2.8以上では、層状ペロブスカイト構造が組みにくい。yが0.2以下では、置換によるNO_x吸収性能の改善がなされにくく、1.5以上では、十分なNO_x吸収性能が得られないことがある。更*



(式中のLnは上記と同じ元素(但し、ストロンチウムを除く)、Bは上記と同じ元素、 $1.8 < x+z < 2.8$ 、 $0 < z < 0.5$ 、 $0.2 < y < 1.5$ 、 $5.5 \leq \delta < 7.0$ を示す。)で表すことができる。この層状ペロブスカイト化合物によれば、一層良好な耐硫黄被毒性、広い温度領域におけるNO_x浄化性能、及び耐久性を実現できる。

【0024】一般式②において、zが0では、NO_x吸収特性が十分には改善されず、0.5を超えると、NO_x吸収特性の著しく劣化することがある。また、x+zは $1.8 < x+z < 2.8$ であるが、この理由は、一般式①におけるxの限定理由と同様である。

【0025】次に、本発明のNO_x浄化触媒材料について説明する。本発明のNO_x浄化触媒材料は、上述の如き層状ペロブスカイト化合物を含有するものである。この層状ペロブスカイト化合物は、酸化雰囲気下においてもNO_xを吸収浄化でき、600℃未満の温度でも優れたNO_x吸収・浄化特性を発揮し、しかも耐硫黄被毒性を有するものである。

【0026】このように、本発明のNO_x浄化触媒材料は、上記層状ペロブスカイト化合物を必須成分とするが、これ以外の他の添加物等を含有することも可能であり、例えば、酸素貯蔵能を有するセリア(CeO₂)、ジルコニア(ZrO₂)、プラセオジウム酸化物(PrO_{2-x})及びこれらの固溶体などを添加することが可能である。

【0027】また、本発明のNO_x浄化触媒材料は、そのままの粉末状で使用することは勿論、粒状やペレット状の各種形状に成形して使用すること、及びアルミナ等の従来の多孔質基材に担持して使用することも可能である。更に、耐火性材料から成るモノリス担体やメタル担体等にコートして使用することも可能であり、特に自動車用排ガス中のNO_xを浄化するに当たっては、ハニカム状担体にコートすることにより、触媒と排ガスとの接触面積を大きくでき、圧力損失も抑制できるため、極めて有効である。

【0028】なお、このハニカム状担体としては、一般にセラミックス等のコーゼライト質のものが多く用いられるが、フェライト系ステンレス等の金属材料から成るハニカム状担体を用いることも可能であり、更には触媒材料粉末そのものをハニカム状に成形してもよい。

*に、δが5.5未満では、層状ペロブスカイト構造が組みにくく、7.0以上でも、層状ペロブスカイト構造が不安定となる。

【0023】また、本発明の層状ペロブスカイト化合物においては、一般式①のLn(ランタノイド)として、少なくともストロンチウムを選択することが好ましく、この場合、一般式①は、次の一般式②

【0029】また、本発明のNO_x浄化触媒材料は、上述如く、酸化雰囲気及び還元雰囲気の双方でNO_xを吸収浄化でき、且つ耐硫黄被毒性にも優れるが、従来公知のPt、Pd及びRh(ロジウム)等の貴金属成分と組み合わせることも可能であり、例えば、Pt及び/又はPdと組み合わせることにより、酸化雰囲気下でのNO_x吸収浄化性能に加えて、還元雰囲気下でのNO_x分解浄化性能を向上させることもできる。

【0030】次に、本発明の排ガス浄化用触媒について説明する。上述の如く、本発明の排ガス浄化用触媒は、多孔質担体に、上記本発明のNO_x浄化触媒材料と、白金及び/又はパラジウムとを担持して成り、酸素過剰雰囲気下における排気ガス中の一酸化炭素(CO)、炭化水素(HC)及び窒素酸化物を同時に浄化し得るものである。

【0031】ここで、白金及び/又はパラジウムの担持は、上述の理由から行うものであるが、これ以外にもロジウム(Rh)等を担持させることができる。この際、多孔質担体としては、上述のようにアルミナなどの公知材料を用いることができ、ハニカム状担体を使用することも言うまでもない。

【0032】また、本発明の排ガス浄化用触媒においては、NO_x浄化触媒材料と白金等の貴金属とを混合してハニカム状担体にコートし、両者を同一の触媒層に担持させてもよいが、両者を分離してコートし、別個の触媒層を成形してもよい。更に、かかる別個の触媒層を積層してもよく、更には、排気ガス流路の上流側及び下流側に分けて配置してもよい。

【0033】

【実施例】以下、本発明を、図面を参照して実施例及び比較例により更に詳細に説明するが、本発明はこれら実施例に限定されるものではない。

【0034】(実施例1)ランタン、バリウム、マンガン及びコバルトの炭酸塩又は水酸化物を出発原料として、各元素の組成比がLa:Ba:Mn:Co=0.8:2.2:1.5:0.5となるように配合し、ボールミルで粉碎混合した。次いで、特開平2-74505号公報に記載された方法と同様の操作により、クエン酸と反応させて複合クエン酸塩粉末を製造した後、900℃で5時間仮焼後、更に大気中に1400℃で10時間焼成して、La_{0.8}Ba_{2.2}Mn_{1.5}Co_{0.5}

$O_{7-δ}$ ($δ$ は約0.4)で示される複合酸化物粉末(層状ペロブスカイト化合物)を得た。得られた複合酸化物粉末(焼成粉)を熱分析装置内に配置し、後述する熱重量分析法によりNOの吸収浄化能を測定し、NOx浄化触媒材料としての性能評価を行った。

【0035】(実施例2)出発原料のコバルトを鉄とした以外は、実施例1と同様の操作を繰り返し、 $La_{0.8}Ba_{2.2}Mn_{1.5}Fe_{0.5}O_{7-δ}$ ($δ$ は約0.3)で示される複合酸化物粉末(層状ペロブスカイト化合物)を得た。上記同様に、熱重量分析法によりNOの吸収浄化能を測定し、NOx浄化触媒材料としての性能評価を行った。

【0036】(実施例3)出発原料のコバルトをアルミニウムとした以外は、実施例1と同様の操作を繰り返し、 $La_{0.8}Ba_{2.2}Mn_{1.5}Al_{0.5}O_{7-δ}$ ($δ$ は約0.3)で示される複合酸化物粉末を得た。上記同様に、熱重量分析法によりNOの吸収浄化能を測定し、NOx浄化触媒材料としての性能評価を行った。

【0037】(実施例4)出発原料の各元素の組成比を $La : Ba : Mn : Co = 1.0 : 2.0 : 1.5 : 0.5$ となるように配合した以外は、実施例1と同様の操作を繰り返し、 $La_{1.0}Ba_{2.0}Mn_{1.5}Co_{0.5}O_{7-δ}$ ($δ$ は約0.4)で示される複合酸化物粉末を得た。上記同様に、熱重量分析法によりNOの吸収浄化能を測定し、NOx浄化触媒材料としての性能評価を行った。

【0038】(実施例5)出発原料の各元素の組成比を $La : Ba : Mn : Co = 1.0 : 2.0 : 1.0 : 1.0$ となるように配合した以外は、実施例1と同様の操作を繰り返し、 $La_{1.0}Ba_{2.0}Mn_{1.0}Co_{1.0}O_{7-δ}$ ($δ$ は約0.3)で示される複合酸化物粉末を得た。上記同様に、熱重量分析法によりNOの吸収浄化能を測定し、NOx浄化触媒材料としての性能評価を行った。

【0039】(実施例6)出発原料の各元素の組成比を $La : Ba : Mn : Co = 0.5 : 2.5 : 1.5 : 0.5$ となるように配合した以外は、実施例1と同様の操作を繰り返し、 $La_{0.5}Ba_{2.5}Mn_{1.5}Co_{0.5}O_{7-δ}$ ($δ$ は約0.4)で示される複合酸化物粉末を得た。上記同様に、熱重量分析法によりNOの吸収浄化能を測定し、NOx浄化触媒材料としての性能評価を行った。

【0040】(比較例1)各元素の組成比を $La : Ba : Mn : Co = 0.2 : 0.7 : 0.5 : 0.5$ となるように配合した以外は、実施例1と同様の操作を繰り返し、 $La_{0.2}Ba_{0.7}Mn_{0.5}Co_{0.5}O_{7-δ}$ ($δ$ は約0.3)で示される複合酸化物粉末を得た。上記同様に、熱重量分析法によりNOの吸収浄化能を測定し、NOx浄化触媒材料としての性能評価を行っ

た。

【0041】(比較例2)各元素の組成比を $La : Ba : Mn : Co = 1.0 : 2.0 : 1.8 : 0.2$ となるように配合した以外は、実施例1と同様の操作を繰り返し、 $La_{1.0}Ba_{2.0}Mn_{1.8}Co_{0.2}O_{7-δ}$ ($δ$ は約0.2)で示される複合酸化物粉末を得た。上記同様に、熱重量分析法によりNOの吸収浄化能を測定し、NOx浄化触媒材料としての性能評価を行った。

10 【0042】(比較例3)各元素の組成比を $La : Ba : Mn : Co = 1.0 : 2.0 : 0.5 : 1.5$ となるように配合した以外は、実施例1と同様の操作を繰り返し、 $La_{1.0}Ba_{2.0}Mn_{0.5}Co_{1.5}O_{7-δ}$ ($δ$ は約0.5)で示される複合酸化物粉末を得た。上記同様に、熱重量分析法によりNOの吸収浄化能を測定し、NOx浄化触媒材料としての性能評価を行った。

20 【0043】(比較例4)各元素の組成比を $La : Ba : Mn : Co : O = 0.2 : 2.8 : 1.5 : 0.5$ となるように配合した以外は、実施例1と同様の操作を繰り返し、 $La_{0.2}Ba_{2.8}Mn_{1.5}Co_{0.5}O_{7-δ}$ ($δ$ は約0.7)で示される複合酸化物粉末を得た。上記同様に、熱重量分析法によりNOの吸収浄化能を測定し、NOx浄化触媒材料としての性能評価を行った。

30 【0044】(比較例5)各元素の組成比を $La : Ba : Mn : Co : O = 1.2 : 1.8 : 1.5 : 0.5$ となるように配合した以外は、実施例1と同様の操作を繰り返し、 $La_{1.2}Ba_{1.8}Mn_{1.5}Co_{0.5}O_{7-δ}$ ($δ$ は約0.3)で示される複合酸化物粉末を得た。上記同様に、熱重量分析法によりNOの吸収浄化能を測定し、NOx浄化触媒材料としての性能評価を行った。

40 【0045】(実施例7)出発原料にネオジムを加え、各元素の組成比を $La : Nd : Ba : Mn : Co = 0.5 : 0.3 : 2.2 : 1.5 : 0.5$ となるように配合した以外は、実施例1と同様の操作を繰り返し、 $La_{0.5}Nd_{0.3}Ba_{2.2}Mn_{1.5}Co_{0.5}O_{7-δ}$ ($δ$ は約0.4)で示される複合酸化物粉末を得た。上記同様に、熱重量分析法によりNOの吸収浄化能を測定し、NOx浄化触媒材料としての性能評価を行った。

50 【0046】(実施例8)出発原料にイットリウムを加え、各元素の組成比を $La : Y : Ba : Mn : Co = 0.7 : 0.1 : 2.2 : 1.5 : 0.5$ となるように配合した以外は、実施例1と同様の操作を繰り返し、 $La_{0.7}Y_{0.1}Ba_{2.2}Mn_{1.5}Co_{0.5}O_{7-δ}$ ($δ$ は約0.4)で示される複合酸化物粉末を得た。上記同様に、熱重量分析法によりNOの吸収浄化能を測定し、NOx浄化触媒材料としての性能評価を行っ

た。

【0047】（実施例9）出発原料にサマリウムを加え、各元素の組成比を $La:Sm:Ba:Mn:Co=0.6:0.2:2.2:1.5:0.5$ となるように配合した以外は、実施例1と同様の操作を繰り返し、 $La_{0.6}Sm_{0.2}Ba_{2.2}Mn_{1.5}Co_{0.5}O_{7-\delta}$ （ δ は約0.4）で示される複合酸化物粉末を得た。上記同様に、熱重量分析法によりNOの吸収浄化能を測定し、NO_x浄化触媒材料としての性能評価を行った。

【0048】（実施例10）出発原料にガドリウムを加え、各元素の組成比を $La:Gd:Ba:Mn:Co:O=0.7:0.1:2.2:1.5:0.5$ となるように配合した以外は、実施例1と同様の操作を繰り返し、 $La_{0.7}Gd_{0.1}Ba_{2.2}Mn_{1.5}Co_{0.5}O_{7-\delta}$ （ δ は約0.5）で示される複合酸化物粉末を得た。上記同様に、熱重量分析法によりNOの吸収浄化能を測定し、NO_x浄化触媒材料としての性能評価を行った。

【0049】（実施例11）出発原料にストロンチウムを加え、各元素の組成比を $La:Sr:Ba:Mn:Co:O=0.5:0.3:2.2:1.5:0.5$ となるように配合した以外は、実施例1と同様の操作を繰り返し、 $La_{0.5}Sr_{0.3}Ba_{2.2}Mn_{1.5}Co_{0.5}O_{7-\delta}$ （ δ は約0.4）で示される複合酸化物粉末を得た。上記同様に、熱重量分析法によりNOの吸収浄化能を測定し、NO_x浄化触媒材料としての性能評価を行った。

【0050】（比較例6）出発原料にストロンチウムを加え、各元素の組成比を $La:Sr:Ba:Mn:Co:O=0.7:0.5:1.8:1.5:0.5$ となるように配合した以外は、実施例1と同様の操作を繰り返し、 $La_{0.7}Sr_{0.5}Ba_{1.8}Mn_{1.5}Co_{0.5}O_{7-\delta}$ （ δ は約0.6）で示される複合酸化物粉末を得た。上記同様に、熱重量分析法によりNOの吸収浄化能を測定し、NO_x浄化触媒材料としての性能評価を行った。

【0051】（実施例12）実施例1の複合酸化物粉末を用いて下記の操作を行い、Pt/La_{0.6}Ba_{2.2}Mn_{1.5}Co_{0.5}O_{7-δ}/アルミナで表されるハニカム触媒を調製した。アルミナ粉末100重量部に、アルミナゾル70重量部、硝酸アルミニウム水溶液（40wt%）15重量部及び水30重量部を加えて攪拌混合し、アルミナスラリーを得た。このアルミナスラリーに実施例1の複合酸化物粉末La_{0.6}Ba_{2.2}Mn_{1.5}Co_{0.5}O_{7-δ}を加えて混合攪拌し、コーティング用スラリーを得た。また、この際、La_{0.6}Ba_{2.2}Mn_{1.5}Co_{0.5}O_{7-δ}粉末の配合量は、触媒完成時において、触媒1L（リットル）あたりに該粉末100gが担持されるように調整し

た。次いで、得られたコーティング用スラリーに、コーゼライト製ハニカム担体を浸漬し、取り出した後、余分なスラリーを吹き払い、80℃で乾燥した後、600℃で1時間焼成した。このようにして造られたハニカム体を2g/Lのジニトロジアミン白金水溶液に浸漬し、250℃で乾燥して本例のハニカム触媒を得た。得られたハニカム触媒は、後述のようにリーン燃焼エンジンの下流の排気流路に配置し、排気ガスの浄化率を測定に供した。

10 【0052】（実施例13）ジニトロジアミン白金水溶液の代わりに硝酸パラジウム水溶液を用いた以外は、実施例12と同様の操作を繰り返し、Pd/La_{0.6}Ba_{2.2}Mn_{1.5}Co_{0.5}O_{7-δ}/アルミナで表される本例のハニカム触媒を得、得られたハニカム触媒の排気ガスの浄化率を上記同様に測定した。

【0053】（比較例7）比較例1の複合酸化物粉末を用いて下記の操作を行い、Pt/La_{0.6}Ba_{0.7}Mn_{0.5}Co_{0.5}O_{3-δ}/アルミナで表される本例のハニカム触媒を調製した。実施例1の複合酸化物粉末の代わりに比較例1の複合酸化物粉末を用いた以外は、実施例12と同様の操作を繰り返し、Pt/La_{0.6}Ba_{0.7}Mn_{0.5}Co_{0.5}O_{3-δ}/アルミナで表されるハニカム触媒を得た。排気ガスの浄化率を上記同様に測定した。

20 【0054】（比較例8）ジニトロジアミン白金水溶液の代わりに硝酸パラジウム水溶液を用いた以外は、比較例7と同様の操作を繰り返し、Pd/La_{0.6}Ba_{0.7}Mn_{0.5}Co_{0.5}O_{3-δ}/アルミナで表されるハニカム触媒を得た。排気ガスの浄化率を上記同様に測定した。

30 【0055】〔試験例〕実施例1～13及び比較例1～8の複合酸化物のNO_x吸収特性を下記の方法で評価した。

【0056】（NO吸収特性評価法）酸化物表面のNO_x吸収量は、以下の条件で熱重量分析を行い、触媒反応によるNO_x吸収に伴う重増減からNO_x吸収量を求めることにより評価した。得られた結果を表1、表2及び図1に示す。

（1）熱分析反応条件

40 1）反応条件（I）

NO:SO₂:N₂=0.500:0.025:99.475の組成ガスを流量100cc/minにて装置中に流入させてNO及びSO₂を吸収させた。

2）反応条件（II）

N₂:SO₂=0.025:99.975の組成である混合ガスを流量100cc/minにて装置中に流入させてSO₂を吸収させた。

50 3）上記各測定から得られたデータを基に酸化物のSO₂吸収量を反応条件（II）により見積もり、

反応条件(1)の測定結果を正味のNO吸収量とし、この測定結果からNO最大吸収温度を求めた。

(2) 測定温度

室温から800℃まで10℃/minの昇温速度で測定した。

【0057】(NO_x浄化特性評価法)所定の複合酸化物触媒材料と貴金属とをハニカム担体に担持した各例の触媒をリーンバーンエンジンの排気系に配置し、エンジンを空燃比A/F=14.5(ストイキ)とA/F=1*

*8(リーン)とを交互に繰り返し変化させて、触媒浄化性能評価を行った。なお、耐久試験では、排ガス中のSO₂濃度が50ppmとなるようSO₂ガスを流入し、入口温度650℃で、A/F=14.5とA/F=18とを交互に変化させて24時間行い、この後に触媒浄化性能評価を行った。得られた結果を表3に示す。

【0058】

【表1】

	層状ペロブスカイト組成	NO最大吸収温度(℃)	NO最大吸収量(Wt.%)
実施例 1	La _{0.8} Ba _{2.2} Mn _{1.5} Co _{0.5} O _{7-δ}	510	3.84
実施例 2	La _{0.8} Ba _{2.2} Mn _{1.5} Fe _{0.5} O _{7-δ}	495	4.62
実施例 3	La _{0.8} Ba _{2.2} Mn _{1.5} Al _{0.5} O _{7-δ}	548	4.23
実施例 4	La _{1.0} Ba _{2.0} Mn _{1.5} Co _{0.5} O _{7-δ}	481	3.57
実施例 5	La _{1.0} Ba _{2.0} Mn _{1.0} Co _{1.0} O _{7-δ}	486	2.16
実施例 6	La _{0.5} Ba _{2.5} Mn _{1.5} Co _{0.5} O _{7-δ}	513	5.17
比較例 1	La _{0.2} Ba _{0.7} Mn _{0.5} Co _{0.5} O _{3-δ}	421	1.34
比較例 2	La _{1.0} Ba _{2.0} Mn _{1.8} Co _{0.2} O _{7-δ}	- (検出されず)	- (検出されず)
比較例 3	La _{1.0} Ba _{2.0} Mn _{0.5} Co _{1.5} O _{7-δ}	- (検出されず)	- (検出されず)
比較例 4	La _{0.2} Ba _{2.8} Mn _{1.5} Co _{0.5} O _{7-δ}	525	1.23
比較例 5	La _{1.2} Ba _{1.8} Mn _{1.5} Co _{0.5} O _{7-δ}	518	1.15

【0059】

※ ※ 【表2】

	層状ペロブスカイト組成	NO最大吸収温度(℃)	NO最大吸収量(Wt.%)
実施例 7	La _{0.5} Nd _{0.3} Ba _{2.2} Mn _{1.5} Co _{0.5} O _{7-δ}	498	3.76
実施例 8	La _{0.7} Y _{0.1} Ba _{2.2} Mn _{1.5} Co _{0.5} O _{7-δ}	516	3.53
実施例 9	La _{0.6} Sm _{0.2} Ba _{2.2} Mn _{1.5} Co _{0.5} O _{7-δ}	538	3.47
実施例 10	La _{0.7} Gd _{0.1} Ba _{2.2} Mn _{1.5} Co _{0.5} O _{7-δ}	544	3.39
実施例 11	La _{0.5} Sr _{0.3} Ba _{2.2} Mn _{1.5} Co _{0.5} O _{7-δ}	512	2.86
比較例 6	La _{0.7} Sr _{0.5} Ba _{1.8} Mn _{1.5} Co _{0.5} O _{7-δ}	501	1.03

【0060】

【表3】

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	初期NO _x 浄化率 (%)	SO ₂ 共存雰囲気中 耐久後NO _x 浄化率 (%)
実施例 12	96	68
実施例 13	95	65
比較例 7	82	48
比較例 8	76	39

【0061】以上のようにして得られた結果から、以下のことが明らかである。NO_x吸収特性評価の結果を表1、表2に示したが、これより本発明の範囲に属する実施例1～11の層状ペロブスカイト複合酸化物は、比較例1～6に比べて、600℃未満の温度領域、酸化雰囲気下及びSO₂ガスの存在下でも高いNO_x浄化能を有することが分かる。また、このNO_x浄化能は、NO₂ガスを反応ガスとして用いた場合にも同様であることは言うまでもない。

【0062】また、SO₂共存下でのNO_x吸収量は、図1及び図2から、同様の層状ペロブスカイト組成であっても、本発明の所定範囲から外れると著しく減少することが明らかである。更に、NO_x浄化特性評価の結果を表3に示したが、これにより、本発明の層状ペロブスカイト化合物と貴金属とを組み合わせるハニカム担体に担持させた本発明の排ガス浄化用触媒の一実施例である実施例12及び13の触媒は、NO_x浄化率が耐久試験後でも初期浄化率に対して3割程度低下するにとどまり、耐久後の浄化率が半減した比較例7及び8に比べて明らかに優れた耐久性を有し、SO₂共存下でも有効に排気ガスを浄化できることが分かる。

【0063】以上、本発明を好適実施例により詳細に説明したが、本発明はこれらに限定されるものではなく、本発明の開示の範囲内で種々の変形が可能である。例えば

＊ば、本発明の層状ペロブスカイト化合物の有効性を、排ガス浄化用触媒を例にとって説明したが、本発明の化合物の用途はこれに限定されるものではなく、層状ペロブスカイト化合物について従来から公知の用途、具体的には、誘電体、磁気抵抗素子、ガスセンサー及び電極、特に固体電解質用電極などに応用できるのは言うまでもない。

【0064】

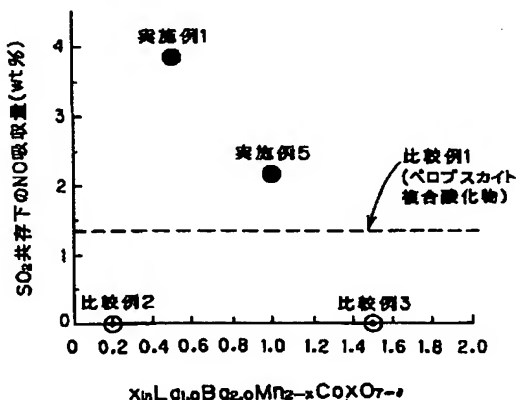
- 20 【発明の効果】以上説明してきたように、本発明によれば、特定の組成・構造を有する新規な層状ペロブスカイト化合物を用いることとしたため、硫黄被毒を生ずる環境下において、600℃未満の温度領域及び酸化雰囲気下でも高いNO_x浄化能を有し、且つ十分な耐硫黄被毒性を有する層状ペロブスカイト化合物、窒素酸化物浄化触媒材料及びこれを用いた排ガス浄化用触媒を提供することができる。

【図面の簡単な説明】

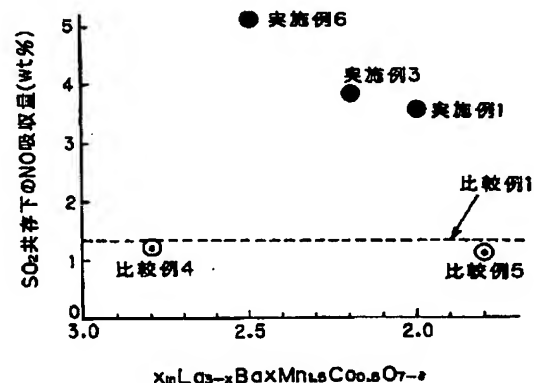
- 【図1】 $\text{La}_{1-x}\text{Ba}_x\text{Mn}_{2-x}\text{Co}_x\text{O}_{7-\delta}$ におけるxとNO吸収量との関係を示す図である。

- 30 【図2】 $\text{La}_{3-x}\text{Ba}_x\text{Mn}_{1.5}\text{Co}_{0.5}\text{O}_{7-\delta}$ におけるxとNO吸収量との関係を示す図である。

【図1】



【図2】



フロントページの続き

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 BA37X BA37Y BB20
 4G002 AA06 AA07 AA08 AA09 AA10
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(54) LAMINAR PEROVSKITE COMPOUND, CATALYST MATERIAL FOR PURIFICATION OF NITROGEN OXIDE AND CATALYST FOR PURIFICATION OF EXHAUST GAS USING THE SAME

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain an oxide having high NO_x detoxifying ability by preparing a laminar perovskite compd. containing at least each one kind of lanthanoid element and 3d transition element, and barium and manganese.

SOLUTION: This laminar perovskite compd. is expressed by formula I or formula II and has high NO_x purifying ability and resistance against sulfur poisoning even in the temp. range of <600° C and in an oxidative atmosphere. In formula I, Ln is a lanthanoid element, B is a 3d transition element, and x, y and δ satisfy $1.8 < x < 2.8$, $0.2 < y < 1.5$ and $5.5 \leq \delta < 7.0$. In formula II, Ln and B are the same elements as in formula I, x, z, y and δ satisfy $1.8 < x+z < 2.8$, $0 < z < 0.5$, $0.2 < y < 1.5$ and $5 \leq \delta < 7.0$. Preferably, Ln is at least one kind selected from lanthanum, neodymium, samarium, gadolinium, yttrium and strontium, and B is at least one kind selected from iron, cobalt and aluminum. The obtd. oxide is deposited on a porous carrier or the like to be used as a catalyst for cleaning of exhaust gas.



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JAPANESE

[JP,2000-256017,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION TECHNICAL PROBLEM MEANS
EXAMPLE DESCRIPTION OF DRAWINGS DRAWINGS

[Translation done.]

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 CLAIMS

[Claim(s)]

[Claim 1] Following general formula $Ln_{3-x}B_xMn_{2-y}ByO_{7-\delta}$ — Stratified perovskite compound characterized by what is expressed with ** (Ln in a formula shows at least one sort of lanthanoids, at least one sort of elements chosen from the group to which B changes from 3d transition element, $1.8 < x < 2.8$, $0.2 < y < 1.5$, and $5.5 \leq \delta < 7.0$).

[Claim 2] The stratified perovskite compound according to claim 1 characterized by for Ln(s) of the above-mentioned general formula ** being at least one sort of elements chosen from the group which consists of a lanthanum, neodymium, samarium, a gadolinium, an yttrium, and strontium, and being at least one sort of elements chosen from the group to which B changes from iron, cobalt, and aluminum.

[Claim 3] Following general formula $Ln_{3-(x+z)}B_xSr_zMn_{2-y}ByO_{7-\delta}$ — Stratified perovskite compound according to claim 1 or 2 characterized by what is expressed with ** (the element (however, strontium is removed) as the above with same Ln in a formula and B show the same element as the above, $1.8 < x+z < 2.8$, $0 < z < 0.5$, $0.2 < y < 1.5$, and $5.5 \leq \delta < 7.0$).

[Claim 4] The nitrogen-oxides purification catalyst ingredient characterized by containing the stratified perovskite compound of a publication in any one term of claims 1-4, and growing into it.

[Claim 5] The catalyst for emission gas purification characterized by supporting a nitrogen-oxides purification catalyst ingredient according to claim 4 and platinum, and/or palladium to porosity support, and growing into it in the catalyst for emission gas purification which can purify the carbon monoxide, the hydrocarbon, and nitrogen oxides in the exhaust gas under a hyperoxia ambient atmosphere to coincidence.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] This invention relates to the catalyst for emission gas purification which used a stratified perovskite compound, a nitrogen-oxides purification catalyst ingredient, and this. Further in a detail The stratified perovskite compound which is a multiple oxide which has specific presentation and structure, and has the property which can carry out absorption purification of NOx under an oxygen ambient atmosphere and reducing atmosphere. It is effective in adsorption, a denitrification process, etc. of NOx which are generated about the nitrogen-oxides purification catalyst ingredient and the catalyst for emission gas purification using this in the chemical process in purification, works, etc. of exhaust gas which are especially discharged by operation of an internal combustion engine or combustion of natural gas.

[0002]

[Description of the Prior Art] Ideally, although the ingredient which has perovskite type structure belongs to cubic system, it takes the structure distorted belonging to tetragonal system, orthorhombic system, hexagonal system, etc. in many cases, and shows various electromagnetic interesting properties — a ferroelectricity is shown for the dipole moment produced by this strain. For this reason, many things are studied as an electromagnetic ingredient from the former, and it inquires as ingredients, such as a dielectric, a magnetic resistance element, a gas sensor and an electrode, especially an electrode for solid electrolytes, and the single crystal of BaTiO₃, KTaO₃, or KNbO₃ grade which is a ferroelectric attracts attention as a charge of electro-optics material.

[0003] The attempt which compounds the perovskite compound which has the property which carried out laminating various perovskite ingredients etc. and was excellent in recent years is also made, and nitrogen oxides are absorbed, and since it decomposes and emits to oxygen and nitrogen, there are some these which attract attention in purification of exhaust gas, so that it may mention later.

[0004] Moreover, as a catalyst which purifies an internal combustion engine's exhaust gas from the former, it calcinates after applying a gamma-alumina slurry to heat-resistant support, such as cordierite, and the three way component catalyst for emission gas purification which supported noble metals, such as platinum (Pt), palladium (Pd), and a rhodium (Rh), is typical, and it is widely known so that it may be represented by the emission-gas-purification catalyst for automobiles.

[0005] Furthermore, the demand level has been going up quality and an amount from the rise of consciousness to the environment in an earth scale in recent years to an improvement of an internal combustion engine's combustion efficiency, the improvement in fuel consumption, purification of exhaust gas, etc. From such a situation, operation in the lean combustion (Lean) field in which improving especially an internal combustion engine's combustion is studied, and it burns by the gaseous mixture of current and hyperoxia is performed briskly, and a catalyst which can fully purify NOx also in this Lean field is desired.

[0006] As an approach of fully purifying NOx also in this Lean field (1) The approach (Machida, Murakami, Kijima; J. Mater. Chem., 4 (1994) 1621) using the zeolite catalyst which purifies NOx using the hydrocarbon under lean atmosphere and in a gaseous phase (HC), and (2) barium oxide, The method (JP,5-511556,A, JP,5-261287,A) of combining a lanthanum oxide and platinum, absorbing NOx under lean atmosphere, and making a three way component catalyst purify NOx of 3 yuan in a field is proposed.

[0007] Moreover, Machida and others has reported that the perovskite multiple oxide expressed with La₂-xBa_xSrCu₂O₆ decomposes and emits this absorbed NO to oxygen and nitrogen at an elevated temperature 600 degrees C or more with absorption of NO in the reference of the above (1). Furthermore, in the reference of the above (2), it is indicated by using for purification of the exhaust gas under a hyperoxia ambient atmosphere combining the NOx absorbent and precious metal catalyst which consist of alkali metal, alkaline earth metal, and rare earth elements that the NOx purification engine performance under a hyperoxia ambient atmosphere is obtained.

[0008] in addition — " — science (Kodansha SAIENTIFIKU, 1998) Tanabe of new ligand field — a passerby — in editorial-supervision Kanno ****, Masaki Shinada, and" edited by Yamaguchi Australia, the electronic structure of a transition-metals compound and a chemical bond are indicated, and the electronic state about a perovskite multiple oxide is especially clarified in Chapter 3 (Fujimori ****).

[0009]

[Problem(s) to be Solved by the Invention] However, in the temperature field 600 degrees C or more, emission became remarkable at adsorption and coincidence of NOx, and the conventional perovskite multiple oxide used by the approach of the above (1) had the technical problem that reduction of an NOx absorbed amount will be produced.

[0010] Moreover, with the conventional emission-gas-purification catalyst concerning the combination of the NOx absorbent and noble metals which consist of the alkali metal used by the approach of the above (2), the technical problem that the alkali-metal component added in order to obtain NOx absorbed amount sufficient by heating durability 650 degrees C or more (support) reacted with support, and deteriorated occurred.

[0011] Furthermore, since sulfur oxide (SOx) gas was contained in the exhaust gas in combustion of a diesel, receiving sulfur poisoning was known, and especially the conventional emission-gas-purification catalyst had the technical problem that sulfur poisoning by SOx gas was remarkable, and the NOx purification engine performance fell remarkably, like [in the case of being the reference of the above

(2)], when a barium oxide etc. bore NO_x absorption.

[0012] In addition, although it was also possible to have stabilized Ba by using above-mentioned barium oxide as a perovskite multiple oxide like $\text{La}_{0.7}\text{Ba}_{0.2}\text{Mn}_{0.5}\text{Co}_{0.5}\text{O}_{3-\delta}$, even if this invention persons were this case, they did the knowledge of the NO_x purification engine performance falling remarkably by SO_x gas. Furthermore, this invention persons did the knowledge also of sulfur poisoning by SO_x gas being also remarkable also in $\text{La}_{2-x}\text{Ba}_x\text{SrCu}_2\text{O}_6$ which Machida and others proposed.

[0013] As mentioned above, with the conventional oxide system catalyst, an NO_x absorbed amount decreases remarkably by sulfur poisoning in the NO_x adsorption using these the outside where an usable temperature field is narrow. For this reason, the emission-gas-purification catalyst ingredient and the catalyst for emission gas purification which demonstrate the NO_x purification engine performance under a broad temperature field and an ambient atmosphere in various operating environments were desired.

[0014] The place which this invention is made in view of the technical problem which such a conventional technique has, and is made into the purpose is to offer the stratified perovskite compound which has high NO_x decontamination capacity also under a less than 600-degree C temperature field and an oxidizing atmosphere, and has sufficient sulfur-proof poisoning nature under the environment which produces sulfur poisoning, a nitrogen-oxides purification catalyst ingredient, and the catalyst for emission gas purification using this.

[0015]

[Means for Solving the Problem] this invention persons came to complete a header and this invention for having NO_x decontamination capacity with the new stratified perovskite compound expensive also under a less than 600-degree C temperature field and an oxidizing atmosphere which has specific presentation and structure, and having sufficient sulfur-proof poisoning nature, and a header and the above-mentioned technical problem being solved, as a result of repeating research wholeheartedly that the above-mentioned technical problem should be solved.

[0016] That is, the stratified perovskite compound of this invention is following general formula $\text{Ln}_{3-x}\text{Ba}_x\text{Mn}_{2-y}\text{ByO}_{7-\delta}$. — It is characterized by what is expressed with ** (Ln in a formula shows at least one sort of lanthanoids, at least one sort of elements chosen from the group to which B changes from 3d transition element, $1.8 < x < 2.8$, $0.2 < y < 1.5$, and $5.5 \leq \delta < 7.0$). Moreover, in this stratified compound, it is desirable that it is at least one sort of elements chosen from the group to which Ln of general formula ** changes from a lanthanum, neodymium, samarium, a gadolinium, an yttrium, and strontium, and they are at least one sort of elements chosen from the group to which B changes from iron, cobalt, and aluminum.

[0017] Moreover, the suitable gestalt of the stratified perovskite compound of this invention is following general formula $\text{Ln}_{3-(x+z)}\text{Ba}_x\text{Sr}_z\text{Mn}_{2-y}\text{ByO}_{7-\delta}$. — It is characterized by what is expressed with ** (the element (however, strontium is removed) as the above with same Ln in a formula and B show the same element as the above, $1.8 < x+z < 2.8$, $0 < z < 0.5$, $0.2 < y < 1.5$, and $5.5 \leq \delta < 7.0$).

[0018] Moreover, the nitrogen-oxides purification catalyst ingredient of this invention is characterized by containing the stratified perovskite compound like **** and changing.

[0019] Furthermore, the catalyst for emission gas purification of this invention is characterized by supporting the nitrogen-oxides purification catalyst ingredient, platinum, and/or palladium like **** to porosity support, and growing into it in the catalyst for emission gas purification which can purify the carbon monoxide, the hydrocarbon, and nitrogen oxides in the exhaust gas under a hyperoxia ambient atmosphere to coincidence.

[0020]

[Embodiment of the Invention] Hereafter, the stratified perovskite compound of this invention is explained to a detail. Like the above, the stratified perovskite compound of this invention Following general formula $\text{Ln}_{3-x}\text{Ba}_x\text{Mn}_{2-y}\text{ByO}_{7-\delta}$ — ** (Ln in a formula shows at least one sort of lanthanoids, at least one sort of elements chosen from the group to which B changes from 3d transition element, $1.8 < x < 2.8$, $0.2 < y < 1.5$, and $5.5 \leq \delta < 7.0$) It is expressed, and has the sulfur-proof poisoning nature which compared and was excellent in the usual perovskite multiple oxide, the copper system stratified perovskite oxide, or the oxide mixed stock NO_x absorption catalyst ingredient, NO_x can be effectively purified also in a less than 600-degree C temperature field, and endurance is also good.

[0021] Here, as Ln (lanthanoids) of general formula **, the combination of La (lanthanum), Nd (neodymium), Sm (samarium), Gd (gadolinium), Y (yttrium) or Sr (strontium), and such arbitration is desirable, and the combination of Fe (iron), Co (cobalt) or aluminum (aluminum), and such arbitration is desirable as B (3d transition element).

[0022] Moreover, it is hard to obtain NO_x absorptivity ability with x [sufficient by 1.8 or less], and hard to construct a stratified perovskite structure or more by 2.8. Or less by 0.2, be hard to do the improvement of the NO_x absorptivity ability according [y] to a permutation, and sufficient NO_x absorptivity ability may not be obtained 1.5 or more. Furthermore, less than by 5.5, it is hard to construct a stratified perovskite structure, and delta becomes unstable [a stratified perovskite structure] 7.0 or more.

[0023] In the stratified perovskite compound of this invention, it is desirable as Ln (lanthanoids) of general formula ** to choose strontium at least. General formula ** in this case Moreover, following general formula $\text{Ln}_{3-(x+z)}\text{Ba}_x\text{Sr}_z\text{Mn}_{2-y}\text{ByO}_{7-\delta}$ — ** (the element (however, strontium is removed) as the above with same Ln in a formula and B show the same element as the above, $1.8 < x+z < 2.8$, $0 < z < 0.5$, $0.2 < y < 1.5$, and $5.5 \leq \delta < 7.0$) It can express. According to this stratified perovskite compound, much more good sulfur-proof poisoning nature, the NO_x purification engine performance in a large temperature field, and endurance are realizable.

[0024] In general formula **, in 0, when an NO_x absorption property is not fully improved but z exceeds 0.5, an NO_x absorption property is remarkable and it may deteriorate. Moreover, although $x+z$ is $1.8 < x+z < 2.8$, this reason of it is the same as the reason for limitation of x in general formula **.

[0025] Next, the NO_x purification catalyst ingredient of this invention is explained. The NO_x purification catalyst ingredient of this invention contains the stratified perovskite compound like ****. This stratified perovskite compound can carry out absorption purification of NO_x under an oxidizing atmosphere, demonstrates NO_x absorption / purification property which was excellent even in the temperature of less than 600 degrees C, and, moreover, has sulfur-proof poisoning nature.

[0026] Thus, although the NO_x purification catalyst ingredient of this invention uses the above-mentioned stratified perovskite compound as an indispensable component, it is possible also for containing other additives other than this etc., for example, can add Seria (CeO₂) which has oxygen storage ability, a zirconia (ZrO₂), PURASEOJIUMU oxides (PrO 2-x), these solid solutions, etc.

[0027] Moreover, it is powdered, and the NOx purification catalyst ingredient of this invention can also be supported and used for the conventional porosity base materials, such as fabricating and using it for the shape of a grain, or the various configurations of a pellet type, and an alumina, as well as the thing as it is to use. Furthermore, it is also possible to use it for them, carrying out a coat to monolith support, metal support, etc. which consist of a fireproof ingredient, and since in purifying NOx in the exhaust gas for automobiles especially the touch area of a catalyst and exhaust gas can be enlarged and pressure loss can also be controlled by carrying out a coat to honeycomb-like support, it is very effective.

[0028] In addition, as this honeycomb-like support, although many things of quality of cordierite, such as ceramics, are generally used, it is also possible to use the honeycomb-like support which consists of metallic materials, such as ferrite system stainless steel, and the catalyst ingredient powder itself may be further fabricated in the shape of a honeycomb.

[0029] moreover, the NOx purification catalyst ingredient of this invention — ****, although the absorption purification of NOx can be carried out on the both sides of like, an oxidizing atmosphere, and reducing atmosphere and being excelled also in sulfur-proof poisoning nature. By it being also possible to use it combining noble-metals components, such as Pt, well-known Pd, well-known Rh (rhodium), etc., conventionally, for example, combining with Pt and/or Pd. In addition to the NOx absorption purification engine performance under an oxidizing atmosphere, the NOx decomposition purification engine performance under reducing atmosphere can also be raised.

[0030] Next, the catalyst for emission gas purification of this invention is explained. Like ****, the catalyst for emission gas purification of this invention supports NO purification catalyst ingredient, and the platinum and/or palladium of above-mentioned this invention to porosity support, grows into it, and can purify the carbon monoxide (CO), the hydrocarbon (HC), and nitrogen oxides in the exhaust gas under a hyperoxia ambient atmosphere to coincidence.

[0031] Although support of platinum and/or palladium is performed from an above-mentioned reason, a rhodium (Rh) etc. can be made to support here besides this. Under the present circumstances, it cannot be overemphasized that well-known ingredients, such as an alumina, can be used as mentioned above, and honeycomb-like support can be used as porosity support, either.

[0032] Moreover, in the catalyst for emission gas purification of this invention, although an NOx purification catalyst ingredient and noble metals, such as platinum, may be mixed, a coat may be carried out to honeycomb-like support and the same catalyst bed may be made to support both, both are separated, a coat may be carried out and a separate catalyst bed may be fabricated. Furthermore, the laminating of this separate catalyst bed may be carried out, and it may divide into the upstream and the downstream of exhaust gas passage further, and you may arrange.

[0033]

[Example] Hereafter, although an example and the example of a comparison explain this invention to a detail further with reference to a drawing, this invention is not limited to these examples.

[0034] (Example 1) By using the carbonate or hydroxide of a lanthanum, barium, manganese, and cobalt as a start raw material, it blended so that the presentation ratio of each element might be set to La:Ba:Mn:Co=0.8:2.2:1.5:0.5, and grinding mixing was carried out with the ball mill. Subsequently, after making it react with a citric acid and manufacturing compound citrate powder by the same actuation as the approach indicated by JP,2-74505,A, the multiple oxide powder (stratified perovskite compound) which calcinates at 1400 degrees C in atmospheric air further after 5-hour temporary quenching by 900 degrees C for 10 hours, and is shown by La_{0.8}Ba_{2.2}Mn_{1.5}Co_{0.5}O_{7- δ} (δ is about 0.4) was obtained. The obtained multiple oxide powder (baking powder) has been arranged in thermal-analysis equipment, the absorption decontamination capacity of NO was measured by the thermogravimetric analysis mentioned later, and the performance evaluation as an NOx purification catalyst ingredient was performed.

[0035] (Example 2) Except having used the cobalt of a start raw material as iron, the same actuation as an example 1 was repeated, and the multiple oxide powder (stratified perovskite compound) shown by La_{0.8}Ba_{2.2}Mn_{1.5}Fe_{0.5}O_{7- δ} (δ is about 0.3) was obtained. Like the above, the absorption decontamination capacity of NO was measured by thermogravimetric analysis, and the performance evaluation as an NOx purification catalyst ingredient was performed.

[0036] (Example 3) Except having made the cobalt of a start raw material into aluminum, the same actuation as an example 1 was repeated, and the multiple oxide powder shown by La_{0.8}Ba_{2.2}Mn_{1.5}aluminum_{0.5}O_{7- δ} (δ is about 0.3) was obtained. Like the above, the absorption decontamination capacity of NO was measured by thermogravimetric analysis, and the performance evaluation as an NOx purification catalyst ingredient was performed.

[0037] (Example 4) Except having blended the presentation ratio of each element of a start raw material so that it might be set to La:Ba:Mn:Co=1.0:2.0:1.5:0.5, the same actuation as an example 1 was repeated, and the multiple oxide powder shown by La_{1.0}Ba_{2.0}Mn_{1.5}Co_{0.5}O_{7- δ} (δ is about 0.4) was obtained. Like the above, the absorption decontamination capacity of NO was measured by thermogravimetric analysis, and the performance evaluation as an NOx purification catalyst ingredient was performed.

[0038] (Example 5) Except having blended the presentation ratio of each element of a start raw material so that it might be set to La:Ba:Mn:Co=1.0:2.0:1.0:1.0, the same actuation as an example 1 was repeated, and the multiple oxide powder shown by La_{1.0}Ba_{2.0}Mn_{1.0}Co_{1.0}O_{7- δ} (δ is about 0.3) was obtained. Like the above, the absorption decontamination capacity of NO was measured by thermogravimetric analysis, and the performance evaluation as an NOx purification catalyst ingredient was performed.

[0039] (Example 6) Except having blended the presentation ratio of each element of a start raw material so that it might be set to La:Ba:Mn:Co=0.5:2.5:1.5:0.5, the same actuation as an example 1 was repeated, and the multiple oxide powder shown by La_{0.5}Ba_{2.5}Mn_{1.5}Co_{0.5}O_{7- δ} (δ is about 0.4) was obtained. Like the above, the absorption decontamination capacity of NO was measured by thermogravimetric analysis, and the performance evaluation as an NOx purification catalyst ingredient was performed.

[0040] (Example 1 of a comparison) Except having blended the presentation ratio of each element so that it might be set to La:Ba:Mn:Co=0.2:0.7:0.5:0.5, the same actuation as an example 1 was repeated, and the multiple oxide powder shown by La_{0.2}Ba_{0.7}Mn_{0.5}Co_{0.5}O_{3- δ} (δ is about 0.3) was obtained. Like the above, the absorption decontamination capacity of NO was measured by thermogravimetric analysis, and the performance evaluation as an NOx purification catalyst ingredient was performed.

[0041] (Example 2 of a comparison) Except having blended the presentation ratio of each element so that it might be set to La:Ba:Mn:Co=1.0:2.0:1.8:0.2, the same actuation as an example 1 was repeated, and the multiple oxide powder shown by

La_{1.0}Ba_{2.0}Mn_{1.8}Co_{0.2}O_{7- δ} (δ is about 0.2) was obtained. Like the above, the absorption decontamination capacity of NO was measured by thermogravimetric analysis, and the performance evaluation as an NO_x purification catalyst ingredient was performed.

[0042] (Example 3 of a comparison) Except having blended the presentation ratio of each element so that it might be set to La:Ba:Mn:Co=1.0:2.0:0.5:1.5, the same actuation as an example 1 was repeated, and the multiple oxide powder shown by La_{1.0}Ba_{2.0}Mn_{1.5}Co_{1.5}O_{7- δ} (δ is about 0.5) was obtained. Like the above, the absorption decontamination capacity of NO was measured by thermogravimetric analysis, and the performance evaluation as an NO_x purification catalyst ingredient was performed.

[0043] (Example 4 of a comparison) Except having blended the presentation ratio of each element so that it might be set to La:Ba:Mn:Co:O=0.2:2.8:1.5:0.5, the same actuation as an example 1 was repeated, and the multiple oxide powder shown by La_{0.2}Ba_{2.8}Mn_{1.5}Co_{0.5}O_{7- δ} (δ is about 0.7) was obtained. Like the above, the absorption decontamination capacity of NO was measured by thermogravimetric analysis, and the performance evaluation as an NO_x purification catalyst ingredient was performed.

[0044] (Example 5 of a comparison) Except having blended the presentation ratio of each element so that it might be set to La:Ba:Mn:Co:O=1.2:1.8:1.5:0.5, the same actuation as an example 1 was repeated, and the multiple oxide powder shown by La_{1.2}Ba_{1.8}Mn_{1.5}Co_{0.5}O_{7- δ} (δ is about 0.3) was obtained. Like the above, the absorption decontamination capacity of NO was measured by thermogravimetric analysis, and the performance evaluation as an NO_x purification catalyst ingredient was performed.

[0045] (Example 7) Neodymium was added to the start raw material, except having blended the presentation ratio of each element so that it might be set to La:Nd:Ba:Mn:Co=0.5:0.3:2.2:1.5:0.5, the same actuation as an example 1 was repeated, and the multiple oxide powder shown by La_{0.5}Nd_{0.3}Ba_{2.2}Mn_{1.5}Co_{0.5}O_{7- δ} (δ is about 0.4) was obtained. Like the above, the absorption decontamination capacity of NO was measured by thermogravimetric analysis, and the performance evaluation as an NO_x purification catalyst ingredient was performed.

[0046] (Example 8) The yttrium was added to the start raw material, except having blended the presentation ratio of each element so that it might be set to La:Y:Ba:Mn:Co=0.7:0.1:2.2:1.5:0.5, the same actuation as an example 1 was repeated, and the multiple oxide powder shown by La_{0.7}Y_{0.1}Ba_{2.2}Mn_{1.5}Co_{0.5}O_{7- δ} (δ is about 0.4) was obtained. Like the above, the absorption decontamination capacity of NO was measured by thermogravimetric analysis, and the performance evaluation as an NO_x purification catalyst ingredient was performed.

[0047] (Example 9) Samarium was added to the start raw material, except having blended the presentation ratio of each element so that it might be set to La:Sm:Ba:Mn:Co=0.6:0.2:2.2:1.5:0.5, the same actuation as an example 1 was repeated, and the multiple oxide powder shown by La_{0.6}Sm_{0.2}Ba_{2.2}Mn_{1.5}Co_{0.5}O_{7- δ} (δ is about 0.4) was obtained. Like the above, the absorption decontamination capacity of NO was measured by thermogravimetric analysis, and the performance evaluation as an NO_x purification catalyst ingredient was performed.

[0048] (Example 10) GADORIMIUMU was added to the start raw material, except having blended the presentation ratio of each element so that it might be set to La:Gd:Ba:Mn:Co:O=0.7:0.1:2.2:1.5:0.5, the same actuation as an example 1 was repeated, and the multiple oxide powder shown by La_{0.7}Gd_{0.1}Ba_{2.2}Mn_{1.5}Co_{0.5}O_{7- δ} (δ is about 0.5) was obtained. Like the above, the absorption decontamination capacity of NO was measured by thermogravimetric analysis, and the performance evaluation as an NO_x purification catalyst ingredient was performed.

[0049] (Example 11) Strontium was added to the start raw material, except having blended the presentation ratio of each element so that it might be set to La:Sr:Ba:Mn:Co=0.5:0.3:2.2:1.5:0.5, the same actuation as an example 1 was repeated, and the multiple oxide powder shown by La_{0.5}Sr_{0.3}Ba_{2.2}Mn_{1.5}Co_{0.5}O_{7- δ} (δ is about 0.4) was obtained. Like the above, the absorption decontamination capacity of NO was measured by thermogravimetric analysis, and the performance evaluation as an NO_x purification catalyst ingredient was performed.

[0050] (Example 6 of a comparison) Strontium was added to the start raw material, except having blended the presentation ratio of each element so that it might be set to La:Sr:Ba:Mn:Co=0.7:0.5:1.8:1.5:0.5, the same actuation as an example 1 was repeated, and the multiple oxide powder shown by La_{0.7}Sr_{0.5}Ba_{1.8}Mn_{1.5}Co_{0.5}O_{7- δ} (δ is about 0.6) was obtained. Like the above, the absorption decontamination capacity of NO was measured by thermogravimetric analysis, and the performance evaluation as an NO_x purification catalyst ingredient was performed.

[0051] (Example 12) The following actuation was performed using the multiple oxide powder of an example 1, and the honeycomb catalyst expressed with Pt/La_{0.8}Ba_{2.2}Mn_{1.5}Co_{0.5}O_{7- δ} / alumina was prepared. The alumina sol 70 weight section, the aluminium nitrate water-solution (40wt%) 15 weight section, and the water 30 weight section were added to the alumina powder 100 weight section, stirring mixing was carried out, and the alumina slurry was obtained. Multiple oxide powder La_{0.8}Ba_{2.2}Mn_{1.5}Co_{0.5}O_{7- δ} of an example 1 was added to this alumina slurry, mixed stirring was carried out, and the slurry for coatings was obtained. Moreover, at this time, the loadings of La_{0.8}Ba_{2.2}Mn_{1.5}Co_{0.5}O_{7- δ} powder were adjusted so that 100g of these powder might be supported by per [catalyst 1L (liter)] at the time of catalyst completion. Subsequently, after having blown off the excessive slurry after being immersed and taking out the honeycomb support made from cordierite to the obtained slurry for coatings, and drying at 80 degrees C, it calcinated at 600 degrees C for 1 hour. Thus, it was immersed in the dinitro diamine platinum water solution of 2 g/L, the built honeycomb object was dried at 250 degrees C, and the honeycomb catalyst of this example was acquired. The acquired honeycomb catalyst has been arranged like the after-mentioned to the exhaust air passage of the lower stream of a river of the Lean combustion engine, and presented measurement with the rate of purification of exhaust gas.

[0052] (Example 13) Except having used the palladium nitrate water solution instead of the dinitro diamine platinum water solution, the same actuation as an example 12 was repeated, and the honeycomb catalyst of this example expressed with Pd/La_{0.8}Ba_{2.2}Mn_{1.5}Co_{0.5}O_{7- δ} / alumina was acquired, and was measured like the above of the rate of purification of the exhaust gas of the acquired honeycomb catalyst.

[0053] (Example 7 of a comparison) The following actuation was performed using the multiple oxide powder of the example 1 of a comparison, and the honeycomb catalyst of this example expressed with Pt/La_{0.2}Ba_{0.7}Mn_{0.5}Co_{0.5}O_{3- δ} / alumina was prepared. Except having used the multiple oxide powder of the example 1 of a comparison instead of the multiple oxide powder of an example 1, the same actuation as an example 12 was repeated, and the honeycomb catalyst expressed with Pt/La_{0.2}Ba_{0.7}Mn_{0.5}Co_{0.5}O_{3- δ} /

alumina was acquired. It measured like the above of the rate of purification of exhaust gas.

[0054] (Example 8 of a comparison) Except having used the palladium nitrate water solution instead of the dinitro diamine platinum water solution, the same actuation as the example 7 of a comparison was repeated, and the honeycomb catalyst expressed with Pd/La_{0.2}Ba_{0.7}Mn_{0.5}Co_{0.5}O_{3-δ} / alumina was acquired. It measured like the above of the rate of purification of exhaust gas.

[0055] The following approach estimated the NO_x absorption property of the multiple oxide of the [example of trial] examples 1-13, and the examples 1-8 of a comparison.

[0056] (NO absorption characterization method) The NO_x absorbed amount on the front face of an oxide performed thermogravimetric analysis on condition that the following, and evaluated it by calculating an NO_x absorbed amount from the heavy increase and decrease accompanying the NO_x absorption by catalytic reaction. The obtained result is shown in Table 1, Table 2, and drawing 1.

(1) Thermal-analysis reaction condition 1 reaction condition (I)

NO:SO₂: Presentation GA of N 2= 0.500:0.025:99.475 SU is made to flow into equipment in flow rate 100 cc/min, and it is ** about NO and SO₂. ** was carried out.

2) Reaction condition (II)

N₂: He is Nagare about the mixed gas which is the presentation of SO 2= 0.025:99.975. It was made to flow into equipment in amount 100 cc/min, and SO₂ was made to absorb.

3) It is a reaction condition about SO₂ absorbed amount of an oxide based on the data obtained from each above-mentioned measurement. It estimates by (II) and is net NO absorption about the measurement result of a reaction condition (I). It considered as the amount and the NO maximum absorption temperature was searched for from this measurement result.

(2) It measured with the programming rate of 10 degrees C / min from a measurement temperature room temperature to 800 degrees C.

[0057] (NO_x purification characterization method) The catalyst of each example which supported a predetermined multiple oxide catalyst ingredient and noble metals to honeycomb support has been arranged in the exhaust air system of a lean burn engine, air-fuel ratio A/F=14.5 (SUTOIKI) and A/F=18 (Lean) are repeated by turns, the engine was changed, and the catalyst purification performance evaluation was performed. In addition, in the durability test, SO₂ gas was flowed so that SO₂ concentration in exhaust gas might be set to 50 ppm, with the inlet temperature of 650 degrees C, A/F=14.5 and A/F=18 were changed by turns, it carried out for 24 hours, and the catalyst purification performance evaluation was performed next. The obtained result is shown in Table 3.

[0058]

[Table 1]

	層状ペロブスカイト組成	NO最大吸収 温度 (℃)	NO最大吸収 量 (Wt. %)
実施例 1	La _{0.8} Ba _{2.2} Mn _{1.5} Co _{0.5} O _{7-δ}	510	3.84
実施例 2	La _{0.8} Ba _{2.2} Mn _{1.5} Fe _{0.5} O _{7-δ}	495	4.62
実施例 3	La _{0.8} Ba _{2.2} Mn _{1.5} Al _{0.5} O _{7-δ}	548	4.23
実施例 4	La _{1.0} Ba _{2.0} Mn _{1.5} Co _{0.5} O _{7-δ}	481	3.57
実施例 5	La _{1.0} Ba _{2.0} Mn _{1.0} Co _{1.0} O _{7-δ}	486	2.16
実施例 6	La _{0.5} Ba _{2.5} Mn _{1.5} Co _{0.5} O _{7-δ}	513	5.17
比較例 1	La _{0.2} Ba _{0.7} Mn _{0.5} Co _{0.5} O _{3-δ}	421	1.34
比較例 2	La _{1.0} Ba _{2.0} Mn _{1.8} Co _{0.2} O _{7-δ}	- (検出されず)	- (検出されず)
比較例 3	La _{1.0} Ba _{2.0} Mn _{0.5} Co _{1.5} O _{7-δ}	- (検出されず)	- (検出されず)
比較例 4	La _{0.2} Ba _{2.8} Mn _{1.5} Co _{0.5} O _{7-δ}	525	1.23
比較例 5	La _{1.2} Ba _{1.8} Mn _{1.5} Co _{0.5} O _{7-δ}	518	1.15

[0059]

[Table 2]

	層状ペロブスカイト組成	NO最大吸収 温度 (℃)	NO最大吸収 量 (Wt. %)
実施例 7	$\text{La}_{0.5}\text{Nd}_{0.3}\text{Ba}_{2.2}\text{Mn}_{1.5}\text{Co}_{0.5}\text{O}_{7-\delta}$	498	3.76
実施例 8	$\text{La}_{0.7}\text{Y}_{0.1}\text{Ba}_{2.2}\text{Mn}_{1.5}\text{Co}_{0.5}\text{O}_{7-\delta}$	516	3.53
実施例 9	$\text{La}_{0.6}\text{Sm}_{0.2}\text{Ba}_{2.2}\text{Mn}_{1.5}\text{Co}_{0.5}\text{O}_{7-\delta}$	538	3.47
実施例 10	$\text{La}_{0.7}\text{Gd}_{0.1}\text{Ba}_{2.2}\text{Mn}_{1.5}\text{Co}_{0.5}\text{O}_{7-\delta}$	544	3.39
実施例 11	$\text{La}_{0.5}\text{Sr}_{0.3}\text{Ba}_{2.2}\text{Mn}_{1.5}\text{Co}_{0.5}\text{O}_{7-\delta}$	512	2.86
比較例 6	$\text{La}_{0.7}\text{Sr}_{0.5}\text{Ba}_{1.8}\text{Mn}_{1.5}\text{Co}_{0.5}\text{O}_{7-\delta}$	501	1.03

[0060]

[Table 3]

	初期NO _x 浄化率 (%)	SO ₂ 共存雰囲気中 耐久後NO _x 浄化率 (%)
実施例 12	96	68
実施例 13	95	65
比較例 7	82	48
比較例 8	76	39

[0061] The following things are clear from the result obtained as mentioned above. Although the result of NO absorption characterization was shown in Table 1 and Table 2, it turns out that the stratified perovskite multiple oxide of the examples 1-11 which belong to the range of this invention from this has high NO_x decontamination capacity compared with the examples 1-6 of a comparison also under a less than 600-degree C temperature field, an oxidizing atmosphere, and existence of SO₂ gas. Moreover, it cannot be overemphasized that this NO_x decontamination capacity is also the same as when NO₂ gas is used as reactant gas.

[0062] Moreover, even if it is the same stratified perovskite presentation, if it separates from the NO_x absorbed amount under SO₂ coexistence from the predetermined range of this invention, its decreasing remarkably is clear from drawing 1 and drawing 2. Furthermore, although the result of NO_x purification characterization was shown in Table 3 By this the catalyst of the examples 12 and 13 which are one example of the catalyst for emission gas purification of this invention which honeycomb support was made to support combining the stratified perovskite compound and noble metals of this invention It turns out that it remains for falling about 30 percent to the rate of initial purification also after a durability test, and the rate of NO_x purification has the endurance which was clearly excellent compared with the examples 7 and 8 of a comparison which the rate of purification after durability reduced by half, and can purify exhaust gas effectively also under SO₂ coexistence.

[0063] As mentioned above, although the suitable example explained this invention to the detail, this invention is not limited to these and deformation various by within the limits of an indication of this invention is possible for it. For example, although the effectiveness of the stratified perovskite compound of this invention was explained taking the case of the catalyst for emission gas purification, the application of the compound of this invention is not limited to this, and, specifically, it cannot be overemphasized from the former about a stratified perovskite compound that well-known it is an application and that it is applicable to a dielectric, a magnetic resistance element, a gas sensor and an electrode, especially the electrode for solid electrolytes, etc.

[0064]

[Effect of the Invention] As explained above, according to this invention, it can write using the new stratified perovskite compound which has specific presentation and structure, and the stratified perovskite compound which has high NO_x decontamination capacity also under a less than 600-degree C temperature field and an oxidizing atmosphere, and has sufficient sulfur-proof poisoning nature under the environment which produces sulfur poisoning, a nitrogen-oxides purification catalyst ingredient, and the catalyst for emission gas purification using this can be offered.

[Translation done.]

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is drawing showing the relation of x and NO absorbed amount in $\text{La}_{1.0}\text{Ba}_{2.0}\text{Mn}_{2-x}\text{Co}_x\text{O}_{7-\delta}$.

[Drawing 2] It is drawing showing the relation of x and NO absorbed amount in $\text{La}_{3-x}\text{Ba}_x\text{Mn}_{1.5}\text{Co}_{0.5}\text{O}_{7-\delta}$.

[Translation done.]

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